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Original Research Article

Acid resistance of palm oil fuel ash and metakaolin ternary blend cement mortar

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ABSTRACT

This paper examines the effects of blend of Palm Oil fuel ash (POFA) and Metakaolin (MK) on the resistance of cement mortar to sulphuric acid (H_2SO_4) attack. Tests were conducted on POFA and MK ternary blended cement mortar immersed in a 3% H_2SO_4 solution for up 180 d. Binaries of POFA/cement and MK/cement as well as plain ordinary Portland cement (OPC) mortar was also tested for comparison. The parameters measured include residual compressive strength and residual mass. Additionally, the microstructures of the specimens were analysed using the X-ray diffraction and Fourier transformed infrared techniques. The residual compressive strengths of the mortar specimens for plain OPC, binary blend of POFA and cement, binary blend of MK and cement, and ternary blend of POFA, MK and cement after 180 d of immersion in the acid solution were 25, 30, 33, and 32%, respectively. Moreover, the corresponding residual masses of the specimens were 39, 52, 58, and 54%. Accordingly, the ternary blended mortar performed better in resisting H_2SO_4 attack than the plain OPC and binary blend of POFA/cement mortars.

1. Introduction

Presently, the utilization of pozzolanic materials for concrete production is booming in construction industry due to the derivable environmental, technical and economic benefits [1]. The use of Palm Oil Fuel Ash (POFA), a siliceous and aluminous material obtained from burning palm oil plant residues for energy production in palm oil industry, as cement replacement material has been established to be favourable for producing strong and durable concrete [2,3]. Durable concrete can withstand the pressure of deteriorating agencies such as sulphates and acids to which concrete may be exposed to during its service life [4]. However, plain ordinary Portland cement (OPC) concrete, being highly alkaline, is not resistant to strong acid attack [5]. Once concrete encountered acid substance, a neutralization reaction between hydrogen ion and $Ca(OH)_2$ in the cementitious materials occurs. This decreases the alkalinity of concrete and causes dissolutions of the hydration products leading to the deterioration of concrete [6].

However, with the inclusion of POFA in concrete, the amount of $Ca(OH)_2$ is reduced and the microstructure is enhanced due to pozzolanic and microfilling effects of POFA. Accordingly, the impermeability and hence the ingress rate of acid solution that exacerbates the deleterious actions of acid on concrete is subdued. Studies [7,8] have shown that the resistance of concrete to hydrochloric acid (HCl) attack was enhanced with the addition of 20–30% POFA. Despite these benefits, the major shortcoming of POFA in concrete is the delay in early strength development due to its low pozzolanic activity that prompts longer curing times [3,9]. Nonetheless, the combined use of POFA and a high pozzolanic material such as metakaolin (MK) to partially replace cement and form a ternary system can compensate for the deficiencies of POFA in concrete. MK, like silica fume improves strength development at early age. Metakaolin was selected in this study in lieu of silica fume due its relative cheapness.

Studies on the acid resistance of binary blend of POFA and cement are available, however; the data on the resistance of ternary blend of POFA, MK and cement to acid are extremely limited. Therefore, this study evaluates the effect of ternary blend of POFA, MK and cement on the resistance of mortar to sulphuric acid attack. Sulphuric acid, commonly found in effluent from chemical industry is an extremely corrosive medium causing not only acid attack on

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Table 1
Chemical compositions of binders.

Binder	Oxides (%)										
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	Cl^-	K_2O	TiO_2	LOI[a]
OPC	19.78	3.90	3.00	63.38	2.00	2.85	0.75	0.01	0.18	–	1.90
POFA	63.70	3.68	6.27	5.97	4.11	1.59	–	0.50	9.15	0.30	7.95
MK	54.70	39.90	1.43	–	0.34	–	–	–	2.58	0.70	1.50

[a] Loss on ignition.

Table 2
Physical properties of binders.

Properties	OPC	POFA	MK
Specific gravity	3.15	2.42	2.19
Median particle size, D_{50} (μm)	15.90	10.89	6.67
Strength activity index (%)	–	98	111

Table 3
Mix proportions of mortars.

Mortar type	OPC (%)	POFA (%)	MK (%)	Sp content (% by weight of binder)	Flow (mm)
OPC/control	100	0	0	0	136
20PF/POFA binary	80	20	0	0	148
20MK/MK binary	80	0	20	0.5	138
10PF10MK/ternary	80	10	10	0	134

Sand to binder ratio, 2.75; water to binder ratio, 0.55.

$Ca(OH)_2$ and calcium silicate hydrate (C–S–H) but also sulphate attack on the aluminate phases [10]. In this study, the resistance was measured in terms of compressive strength loss and mass loss. The mineralogical compositions of the specimens after acid attack were also analysed by the Fourier Transformed Infrared (FTIR) spectroscopy and X-ray diffraction (XRD) techniques.

2. Materials and methods

2.1. Materials

OPC, POFA and MK were used as binders. The POFA was collected from a palm oil factory situated in Kilang Sawit PPNJ Kahang, Johor, Malaysia. POFA was ground using a grinding machine to increase its fineness hence its pozzolanic activity. Unground POFA has a large particle size with porous texture that makes it unsuitable for cement substitution [11]. Therefore, the grinding of POFA was necessary. The MK was prepared through the calcination of local kaolin at temperature of 650 °C for 1 h. The kaolin (KM40, brand name) was supplied by the Kaolin (Malaysia) company, Malaysia. Tables 1 and 2 present the chemical compositions and physical properties of the binders, respectively. Based on the chemical compositions and physical properties requirements stipulated in the ASTM standard [12], the MK and POFA used in this study can be classified as Class N and Class F pozzolan, respectively. River sand having a fineness modulus of 2.83, specific gravity of 2.65, and maximum size of 1.18 mm was used as fine aggregate for mortar production. A polycarboxylic ether based superplasticizer (GLENIUM ACE 388) was also used to adjust the mortar flow.

2.2. Preparation of mortars

In this study, four different mortar specimens produced in accordance with the ASTM standard [13] were used. The mortar containing 100% plain OPC represents the control specimen. While the remaining three specimens produced by substituting 20% OPC (by weight) with POFA, MK and combined POFA and MK were labelled as binary blend of POFA and cement (20PF), binary blend of MK and cement (20MK) and ternary (10PF10MK), respectively. Water to binder ratio of 0.55 and sand to binder ratio of 2.75 were kept constant for all the mixes. Superplasticizer was added to maintain the flow for the entire mixes within the same range of 135 ± 10 mm. The mix proportions for the entire specimens are presented in Table 3. After 24 h of casting, the mortar specimens were demoulded and then cured in limewater for 28 d.

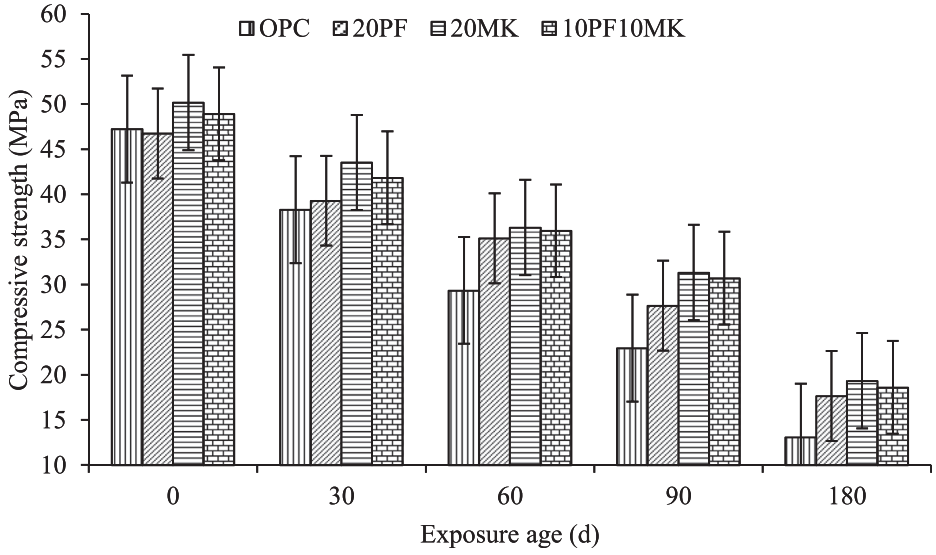

Fig. 1. Compressive strength of mortar after immersion in 3% H_2SO_4 solution.

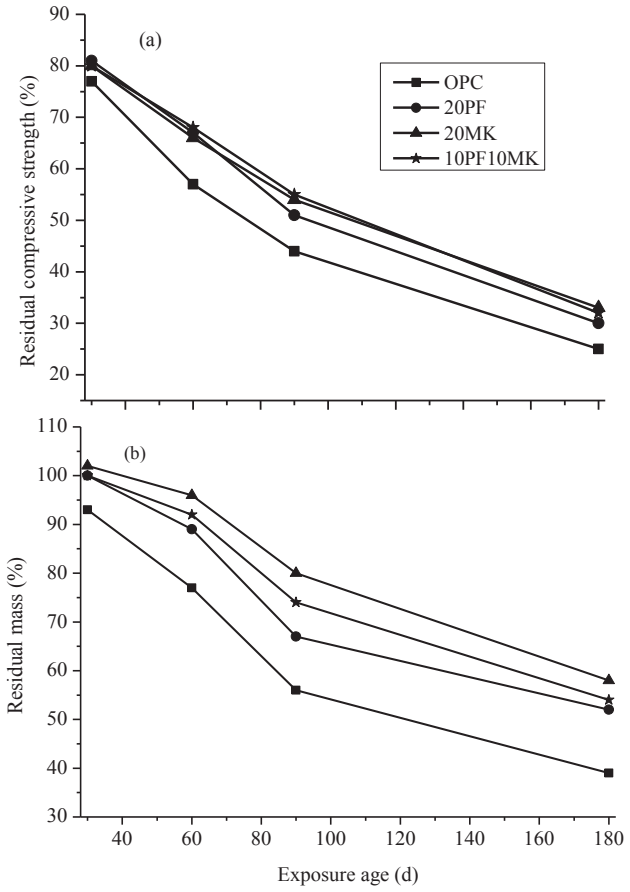

Fig. 2. Parameter profiles of mortar after immersion in 3% H_2SO_4 solution. (a) Residual compressive strength (b) residual mass.

2.3. Methods

2.3.1. Sulphuric acid resistance test

The resistance to sulphuric (H_2SO_4) acid attack test on the mortar specimens was conducted based on the ASTM standard [14]. The parameters investigated were the residual compressive strength and mass of the specimens after exposure. Cube specimens of 50 x 50 × 50 mm size were used. After the initial 28 d of curing in limewater, the specimens were totally immersed in 3% H_2SO_4 (pH ≈ 0.6) solutions while their companions were left in saturated limewater for comparison. The concentration of 3% sulphuric acid was selected to simulate the aggressive environment of sewer and treatment structure [15]. To maintain its concentration, the acid solution was regularly refreshed after every two weeks. The measurements of residual mass and the compressive strength test were carried out at the ages of 30, 60, 90, 120 and 180 d. For the residual mass test, the mass of the specimens before immersion in the acid solution was taken and recorded as the initial mass (M_I). After immersion at every designated age (n), the mass of the specimens was also taken and recorded as M_n. Subsequently, the residual mass (M_{Res}) was calculated using Eq. (1). However, before weighing and the strength test, the specimens removed from solutions were gently rinsed with tap water and then air dried for about 3 h in the laboratory. Three identical specimens were used for each test.

$$M_{\mathrm{Res}} = \frac{M_i - M_n}{M_i} \times 100 \quad (1)$$

2.3.2. XRD and FTIR spectroscopy

The change in hydration products of the specimens after 180 d in acid solution in comparison with those cured in limewater was examined using the XRD and FTIR techniques. Specimens for the test, obtained from the remnant of the crushed specimens used for compressive strength test were prepared by oven drying at 60 °C to a constant mass and then ground to powder passing a 45 μm sieve. XRD measurements were performed on the specimens using the D8 advance Bruker diffractometer with Cu K_α radiation (λ = 1.54 Å). The specimens were scanned over the range of 10–50° (2θ) with a step of 2θ = 0.020° and time per step of 15.4 s. The FTIR spectra of the specimens were generated using a Perkin Elmer Instrument (Spectrum One) FTIR spectrometer in the range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} over an accumulation of 16 scans. About 1 mg of the sample was mixed with 100 mg of Potassium Bromide in an agate mortar and then pressed using a pellet die under pressure to prepare a transparent disk (pellet) for the FTIR test. Nitrogen gas was used to purge the spectrometer chamber.

3. Results and discussion

3.1. Compressive strength change

The compressive strengths and the relative compressive strengths of the mortars after immersion in the acid solution are presented in Figs. 1 and 2a, respectively. The relative strength was obtained with reference to the companion specimens cured in saturated limewater. It is observed that the compressive strength for all the mortar types gradually decreased with increasing exposure periods. However, the rate of strength decrease was successively lower for the blended mortars compared to plain OPC mortar. Generally, the binary of MK and cement mortar followed by the ternary mortar (10PF10MK) showed higher resistance to sulphuric acid attack at all exposure periods than the POFA/cement binary and control mortars. After 180 d of exposure, the compressive strength of mortars of plain OPC, 20PF, 20MK and 10PF10MK as shown in Fig. 2 decreased to 25, 30, 33 and 32%, respectively. The higher resistance to sulphuric acid attack of MK/cement binary and ternary mortars compared to that of POFA/cement binary and control can be related to the higher pozzolanic activity of MK resulting in the formations of more hydrates that refine the microstructures and hence reduces the rate of acid solution ingress into the mortar. This result is in line with the effects of other pozzolanic materials such as rice husk ash, fly ash and silica fume in ternary blended forms that show improvement in acid resistance compared to plain OPC concrete [4,16].

3.2. Residual mass

In addition to compressive strength loss, residual mass is also broadly accepted as an indicator for assessing the resistance of cement based materials to acid attack [17]. The residual masses of plain and blended mortar specimens immersed in the acid solution are shown in Fig. 2b. It is clear that all the mortars with the exception of that of plain OPC showed no reduction in mass after the first 30 d of exposure in the acid solution. Subsequently, there was a continuous reduction in mass for both the plain and blended mortar specimens with increasing exposure time. However, the rate of reduction varies with the mortar type. The mass reduction of the mortar specimens is due to the partial leaching out of bulk cement paste as the result of the dissolution action of sulphuric acid on the cement paste. Sulphuric acid dissolves cement hydrates through neutralization reaction. In a similar pattern to the case of

compressive strength, the MK/cement binary and the ternary specimens show a lesser reduction in mass than that of POFA/cement binary at all ages. In contrast, the plain OPC mortar exhibited the highest reduction in mass. For instance, at 180 d, the residual mass of OPC, 20PF, 20MK and 10PF10MK mortar specimens were 39, 52, 58 and 54%, respectively.

3.3. Residual compressive strength and residual mass relation

The relationships between the residual mass and the change in compressive strength experienced by the mortars due to acid attack are shown in Fig. 3. It is clear that compressive strength dropped as mass loss increased. This directly proportional correlation indicates that the immersion of mortar specimens in sulphuric acid solution results in loss of cement paste and its structural integrity. Also, the immersion in acid causes the weakening of the mortar paste and a reduction in the specimen's size. A regression analysis of the data shown in Fig. 3 reveals a linear trend with correlation coefficients (R^2) ranging from 0.973 to 0.988 depending on the mortar type. Furthermore, the best fit line shown in Fig. 3a suggests that the rate of compressive strength loss with respect to mass loss of the plain OPC mortar due to sulphuric acid is about 1.072 which is higher than those of blended mortars. However, the corresponding rates for the POFA/cement binary, MK/cement binary and ternary mortars are 0.990, 0.977 and 0.974 as shown in Fig. 3b–d, respectively. Impliedly, the rate of deterioration of ternary mortar due to sulphuric acid attack is lower compared to control and the binary mortars.

3.4. XRD analysis

The XRD patterns of the specimens after 180 d in limewater and acid solution are shown in Fig. 4. As shown in Fig. 4a, all the specimens in limewater exhibited the presence of calcium hydroxide ($Ca(OH)_2$) and calcite as the crystalline products of hydration. The calcite was formed as the result of the reaction between calcium hydroxide and atmospheric CO_2 during curing since there is no other source of limestone in the mixture. However, the amount of $Ca(OH)_2$ in the blended specimens was significantly lower than that of plain OPC due to pozzolanic reaction as reflected by the intensity of peak for $Ca(OH)_2$ at $2\theta = 18.9^\circ$.

By comparing Fig. 4a and b, it can be observed that after immersion in the acid solution, the peak for $Ca(OH)_2$ completely disappeared and a new peak for gypsum, $CaSO_4 \cdot 2H_2O$, at $2\theta = 11.7^\circ$ appeared in the plain OPC specimen. However, for the blended mortars in the acid solution, the peaks for gypsum and the weak peaks for $Ca(OH)_2$ were also detected. Considering the intensity of the peak for $Ca(OH)_2$ at $2\theta = 18.9^\circ$ as a criterion, the relative amount of $Ca(OH)_2$ in the specimens immersed in the acid solution follows the order: OPC < 20PF < 10PF10MK < 20MK. Similarly, taking the diffraction peak for $CaSO_4 \cdot 2H_2O$ at $2\theta = 11.7^\circ$ as a measure, the amount of $CaSO_4 \cdot 2H_2O$ in the specimens immersed in acid solution follows the order of OPC > 20PF > 10PF10MK > 20MK. According to Chen et al., this order, which can be related to the rate of deterioration of sulphuric acid on cementitious materials indicates that the combined use of MK and POFA shows a better resistance to sulphuric acid attack than when POFA is singly used. Hence, the higher residual compressive strength and residual mass of the ternary mortar compared to plain OPC and binary POFA/cement mortars can be understood.

3.5. FTIR analysis

The FTIR spectra of the control and blended mortars specimens in limewater for 180 d are shown in Fig. 5a. The peaks at 3645 cm^{-1} is due to O–H stretching vibrations related to $Ca(OH)_2$ while the asymmetric Si–O stretching band (v_3) at 973 to 980 cm^{-1} and the in-plane Si–O bending vibrations (v_2) at 459 to 464 cm^{-1} indicate the formation of polymerized calcium silicate hydrates (C–S–H). The C–O stretching (v_3) and bending (v_2) bands at 875 and

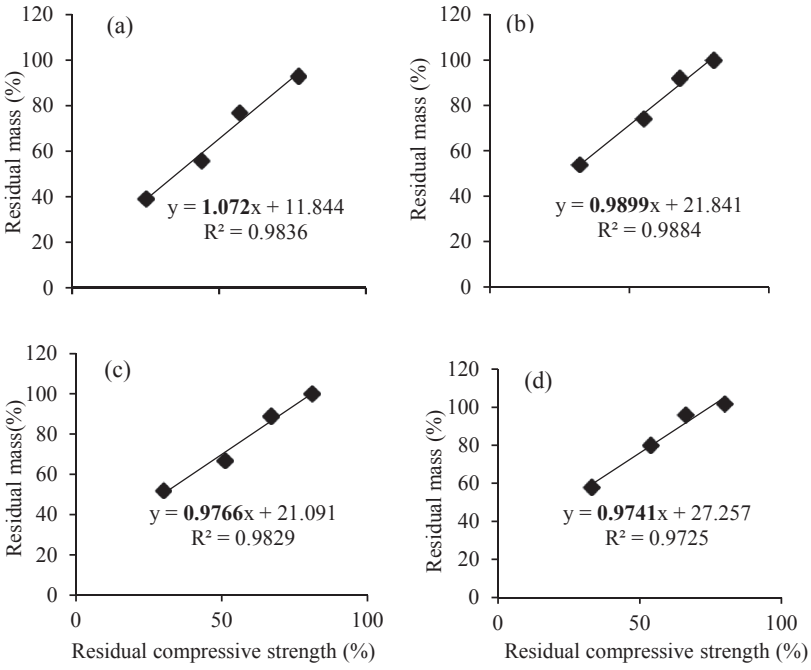

Fig. 3. Relationship between residual compressive strength and residual mass of mortars exposed to acid (a) OPC, (b) 20PF, (c) 20MK, and (d) Ternary.

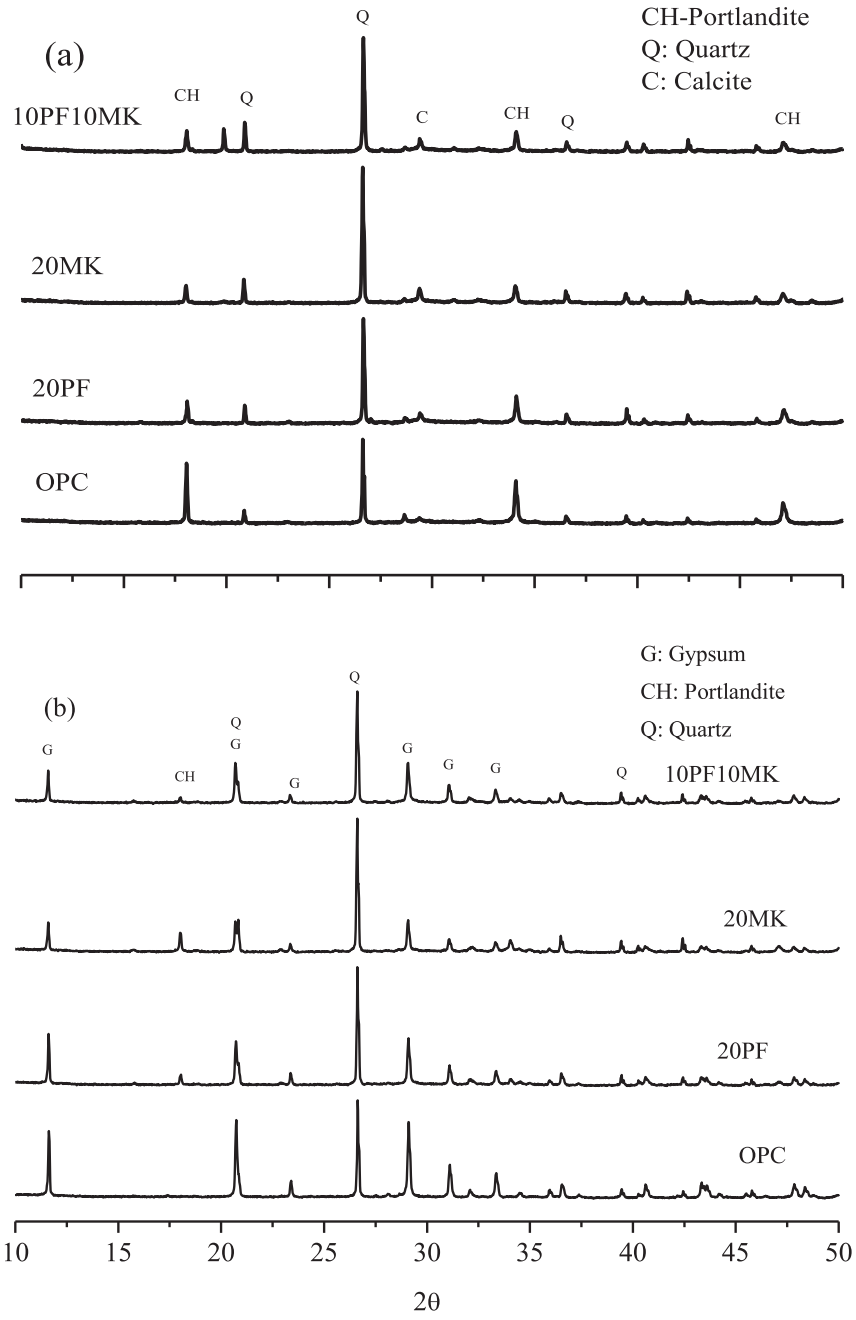

Fig. 4. XRD patterns of mortars after 180 days in (a) limewater (b) 3% H_2SO_4 solution.

1424 cm^{-1}, respectively are assigned to the calcite ($CaCO_3$). Additionally, the broad band detected at 3435 cm^{-1} is due to symmetric and anti-symmetric stretching vibration of water bond in the hydration products. These band assignments tallied with those reported in previous literature [18–20].

In comparison to the specimens immersed in acid solution as shown in Fig. 5b, it can be seen that most of the peaks associated with CSH gel, calcite and portlandite disappeared and those related to gypsum dominated the spectra. The gypsum is characterised by the asymmetric water stretching bands at 3541–3552 cm^{-1} and 3399–3402 cm^{-1}, the in-plane bending bands at 1622 and 1685 cm^{-1} associated with water of crystallization, the SO_4^{2-} asymmetric stretching at 1119–1138 cm^{-1} and the v_4 mode of SO_4^{2-} at 669 and 602 cm^{-1}. These absorption bands for gypsum are equally reported by others [6,19]. The appearance of peaks assigned to gypsum further confirms the sulphuric acid attack on the mortars with gypsum as the main corrosion product. The relative increase in the quantity of gypsum in the mortars reflected by their corresponding intensities of peaks at 1685 and 1622 cm^{-1} follows the order of OPC < 20PF < 10PF10MK < 20MK. The lesser content of gypsum in the blended specimens is related to the consumption of portlandite due to pozzolanic reaction that contributes to their better performance in resisting sulphuric acid attack than the control specimen. These results validate the XRD results.

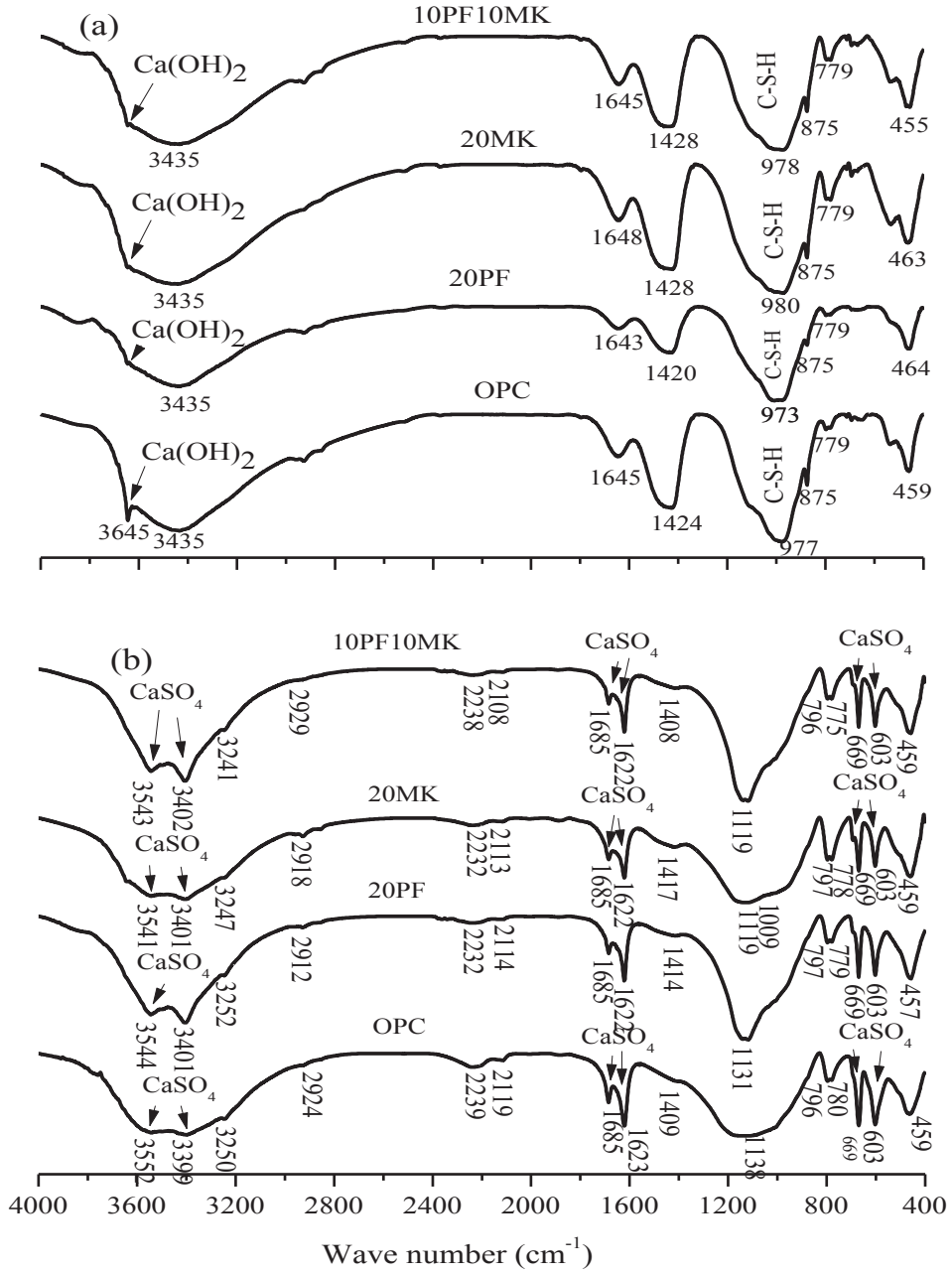

Fig. 5. FTIR spectra of mortars after 180 days in (a) limewater (b) 3% H_2SO_4 solution.

4. Conclusions

Based on the results obtained from this study the following conclusion can be drawn: The reductions in mass and compressive strength of cement mortars made with the ternary blend of POFA, MK and cement due to sulphuric acid attack was lower compared to that of binary blend of POFA and cement, which was also lower than that of plain OPC mortar. Besides, the higher resistance of the ternary mortar than the binary blend of POFA and cement can be attributed, as demonstrated by the XRD and FTIR results, to the lesser formation of gypsum in the system as the results of the reduction of calcium hydroxide due to the higher pozzolanic activity of MK. Therefore, the ternary blend of POFA, MK and cement can be considered beneficial for use in acidic environment.

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